

INTERMOLECULAR PHOTOREACTIONS AND SELECTIVITY
STUDIES IN CONFINED SPACE OF Y ZEOLITES

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INTERMOLECULAR PHOTOREACTIONS AND SELECTIVITY STUDIES
IN CONFINED SPACE OF CATION-EXCHANGED Y ZEOLITES

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For my family, teachers and friends.

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ABSTRACT

Photochemistry in organized assemblies has attracted considerable attention because of their potential use in controlling photophysical and photochemical behaviour of organic molecules in a confined space. Conversion of a starting material to product in a photoreaction involves selectivity by the reaction cavity to the specified product. For solid and rigid media like zeolite, the size of the reaction cavity plays an important role in products selectivity. The surface of NaY zeolite was first studied with paramagnetic probe using Electron Spin Resonance spectroscopy (ESR). Two favourable active sites were identified. The study of a confine space reaction was first studied in the photosensitization of triethylamine by acetophenone in NaY zeolite. ESR result showed that radical cation of amine dimer was formed inside zeolite resulted from the confinement effect of the zeolite Y supercage. Ultra-violet (UV) irradiation of acetophenone in toluene solution results in photochemical hydrogen abstraction and yielded a mixture of both symmetric (1,2-diphenylethane and 1,2-diphenylethyl alcohol) and asymmetric (1,2-diphenylpinacol) coupling products. These were identified and characterized by gas chromatography-mass spectrometry (GC-MS) and nuclear magnetic resonance (NMR). With the introduction of NaY zeolite, high yield of asymmetric product, 1,2-diphenylpinacol was observed. It further proved the confinement effect played by the zeolite produced a drastic change in product selectivity compared to homogenous reaction. Photodimerization of 2-cyclohexenone in various cation-exchanged Y zeolites were also studied in solid state and zeolite-solvent slurries. Both the reactions showed a great reversal of head-to-tail (HT) cyclohexenone dimer, to head-to-head (HH) cyclohexenone dimer with increasing pattern from LiY to CsY zeolite. The study of regioselectivity in the photocycloaddition of 2-cyclohexenone to vinyl acetate was also carried out in zeolite slurries, in which the result showed a drastically change of product yield compared to the homogeneous reaction. However, the cation-exchanged zeolites failed to control the selectivity. This is explained by the passive cavity effect of zeolite.

ABSTRAK

Fotokimia di dalam media teraturapi telah banyak menarik perhatian kerana potensinya dalam mengawal sifat fotofizik dan fotokimia molekul organik dalam ruang terhad. Pengubahan bahan pemula kepada produk dalam tindak balas fotokimia melibatkan kepilihan kaviti tindak balas terhadap produk tertentu. Untuk pepejal tegar seperti zeolit, saiz kaviti tindak balasnya memainkan peranan dalam kepilihan produk. Permukaan zeolite NaY telah dikaji dengan prob paramagnet menggunakan spektroskopi Resonans Spin Elektron (RSE). Dua tapak aktif telah dikenalpasti. Tindak balas dalam ruang terhad pada mulanya telah dikaji dalam pemfotopekaan trietilamina oleh asetofenon dalam zeolit NaY. Keputusan RSE menunjukkan radikal kation dimer amina terbentuk dalam zeolit disebabkan oleh kesan ruang terhad supersangkar zeolit. Penyinaran ultra-lembayung (UL) ke atas asetofenon dalam pelarut toluena pula menyebabkan pengabstrakan hidrogen dan menghasilkan campuran kedua-dua hasil gandingan simetri (1,2-difeniletana dan 1,2-difeniletal alkohol) dan tidak simetri (1,2-difenilpinakol). Pengenalpastian dan pencirian hasil ini seterusnya dilakukan menggunakan kromatografi gas-spektrometri jisim (KG-SJ) dan resonans magnet nukleus (RMN). Penggunaan zeolit NaY pula menghasilkan hasil utama tidak simetri, 1,2-difenilpinakol. Ini membuktikan bahawa ruang terhad pada zeolit telah mengubah kepilihan hasil tersebut berbanding dengan tindak balas homogen. Pemfotodimeran 2-sikloheksenon dalam pelbagai zeolit Y tertukar kation juga dikaji dalam fasa pepejal dan buburan zeolit-pelarut. Kedua-dua tindak balas menunjukkan keterbalikan daripada dimer sikloheksenon kepala-ekor kepada dimer sikloheksenon kepala-kepala dengan penambahan corak daripada zeolit LiY kepada CsY. Seterusnya, keregiopilihan dalam pemfototambahan 2-sikloheksenon kepada vinil asetat telah dijalankan dalam buburan zeolit. Keputusan menunjukkan perubahan besar dalam kepilihan produk berbanding dengan tindak balas homogen. Kegagalan zeolit tertukar kation dalam mengawal kepilihan produk adalah disebabkan oleh kesan kaviti pasif zeolit.

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LIST OF SYMBOLS/ABBREVIATIONS

A	-	Ampere
Å	-	Meter ⁻¹⁰
AcP	-	Acetophenone
cm	-	Centimeter
CH	-	2-Cyclohexenone
Cps	-	Count per second
Eq.	-	Equation
EtOAc	-	Ethyl acetate
g	-	Gram
HH	-	Head-to-head
HT	-	Head-to-tail
Hz	-	Hertz (Second ⁻¹)
¹ H NMR	-	Proton Nuclear magnetic Resonance
FAU	-	Faujasite zeolite
K	-	Kelvin
k	-	Kilo
L	-	Litre
M	-	Mol/Litre
M ⁺	-	Molecular ion

MY	-	Alkali metals Y zeolite
m	-	multiplet
min	-	Minute
mg	-	Milligram
mL	-	Millimeter
mT	-	Millitesla
m/z	-	mass per charge
N	-	Normality
R_f	-	Retention factor
R_t	-	Retention time
s	-	singlet
sec	-	Second
TEA	-	Triethylamine
THF	-	Tetrahydrofuran
V	-	Volt
VA	-	Vinyl acetate
W	-	Watt

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CHAPTER 1

INTRODUCTION

Zeolites have been an object of scientific research and a material beneficial to mankind for more than two centuries since its discovery in 1756. However, it was not until 10-15 years ago that zeolites attracted the keen interest of photochemists who wanted to use them in their research. Photochemists are most interested in controlling chemical reactions with the aid of supramolecular assemblies, aimed at constructing artificial photosynthetic systems, controlling chirality and inventing nanoscale advanced materials. Zeolites are found to be particularly useful for such purpose since they can host various organic molecules in their cavities and channels; such inclusions have often been shown to modify the photophysicals and photochemistry of a given species. Besides, photochemical reactions pursued in zeolites also provide product distributions considerably different from those in solution [1].

Zeolite nanospace could be considered as “hard” because of the frameworks of zeolite are rigid, and “active” because of the non-bonding interaction between the walls of the supercage and the included molecules. On top of these, the most desirable property of zeolite is that it is transparent to light in the near-UV and visible regions. Thus it eliminates the possibility of competitive absorption between the medium and the guest molecule presents [2].

The synthetic utility of intermolecular photodimerization of cyclic enones and the cycloaddition to unsymmetrical alkenes can be limited by the formation of the mixtures of the head-to-head (HH) and head-to-tail (HT) regioisomers [3, 4]. HT

regioisomers are always formed in much larger amount compared to HH isomer in solution reaction [5, 6]. In this research, cation-exchanged Y zeolites were applied to control the regioselectivity of photoproducts in photoreactions of 2-cyclohexenone.

1.1 Objectives of the Research

The objective of this research is to evaluate the feasibility of using zeolite as reaction medium to carry out intermolecular organic photoreactions, i. e. photocycloaddition and photodimerization. This could be further divided to two:

- (i) To compare the products selectivity of between the conventional homomogenous photoreactions with solid state and/or slurry photoreactions in zeolite supercage
- (ii) To utilize the cation-exchanged property of zeolite to control the regioselectivity of desired photoproducts.

Faujasite-Y zeolite was used as host because it possesses large supercages volume which enable us to study a variety of photochemical reactions.

1.2 Scope of the Studies

At the first part of this research, locations of the paramagnetic probe in different adsorption sites of NaY zeolite were studied using Electron Spin Resonance Spectroscopy (ESR). Most of the research in the supramolecular photochemistry within zeolites deal with the intramolecular reaction. In order to study the different approaches used in the intermolecular photoreaction, we have studied the triplet sensitization technique and “spectator” method. The triplet sensitization technique had been applied in the dimerization of triethylamine (TEA) within Y zeolite, while

the “spectator” method was used in gaining selective asymmetric coupling products in the hydrogen abstraction of toluene by acetophenone (AcP).

After gaining experiences from the first part, we turned to the next part, the utilization of the size constriction effect and cation-guest interactions of the cation-exchanged zeolites to modify the selectivity of the regioisomers in photodimerization of 2-cyclohexenone (CH) and photocycloaddition of CH to vinyl acetate (VA).

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